CHARACTERISTICS OF BIODIESEL PRODUCED FROM PALM OIL VIA BASE CATALYZED TRANSESTERIFICATION

CADENCE ISIS TAY

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ABSTRACT

The depletion of petroleum has prompted the global oil industry to look at an alternative source for fuel from renewable energy source, one of which is biodiesel. Biodiesel is a notable alternative to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural resources such as palm oil, soybeans, rapeseeds, coconuts and even recycled cooking oil, and thus reduces dependence on diminishing petroleum fuel. Interest in biodiesel has been expanding recently due to government incentives and high petroleum prices. The majority of biodiesel today is produced via base-catalyzed transesterification with methanol. In order to find the optimal values of biodiesel yield, it is suggested to find the optimum reaction temperature, reaction time and the methoxide:oil ratio. In this study, the parameters were: reaction temperature of 40, 50, and 60 (°C); reaction time of 40, 50 and 60 (minutes); and methanol to oil ratio of 4:1, 6:1, and 8:1. For every experiment done, raw CPO was treated with magnesium sulphate to remove excess moisture then heated at 50 °C and mixed with methoxide (potassium hydroxide and methanol) according to the considered parameters. The agitation speed was set at 250 rpm. After the transesterification process was completed, the hot mixture was left to settle for at least 12 hours in a separator funnel. As soon as the separation was done, two layers were formed, the lower layer of glycerine and the upper layer of palm oil methyl ester. The product of palm oil methyl ester was washed with 70 °C hot tap water for few times. The final product of biodiesel was transferred to a heated oven at 50 °C to remove excess water. The optimum biodiesel yield from the research was 88 % at methoxide:oil ratio of 6:1, time of 60 minutes and temperature of 60 °C. These parameters were chosen as optimum because it is cost effective regarding time and chemical consumption. According to the result, around 500 mL of biodiesel was produced and homogenised to be used in the physical properties tests. The tests showed the properties of biodiesel produced with density of 876.0 kg/m^3, kinematic viscosity of 4.76 mm^2/s, *cetane* number of 62.8, flash point of 170 °C, cloud point at 13°C, pour point at 17 °C and saponification value 206.95 mg/L. The physical properties biodiesel produced showed that the properties are accepted within ASTM D6751 and European Standards.

Keywords: Biodiesel, palm oil, base catalyzed, transesterification

ABSTRAK

Penyusutan bahan api petroleum telah mendorong industri minyak global untuk mencari sumber-sumber alternatif bahan api daripada sumber tenaga yang boleh diperbaharui yang mana salah satunya adalah biodiesel. Biodiesel merupakan bahan api alternatif yang penting kepada petroleum diesel dan digunakan secara meluas kerana ia boleh dihasilkan daripada sumber-sumber semulajadi seperti minyak sawit, kacang soya, kelapa dan juga minyak masak kitar semula. Secara langsung, ia mengurangkan kadar penggunaan bahan api petroleum daripada sumber asing. Peningkatan minat terhadap penyelidikan biodiesel telah berkembang selaras dengan insentif kerajaan dan harga petroleum yang semakin melambung tinggi. Majoriti biodiesel kini dihasilkan melalui proses *base catalyzed transesterification* dengan metanol. Untuk memperoleh nilai optima biodiesel yang terhasil, adalah penting untuk mengkaji nilai optima suhu tindakbalas, masa tindakbalas dan nisbah methanol kepada minyak. Dalam kajian ini, parameter yang ditentukan adalah suhu tindakbalas pada 40 , 50, dan 60 (°C); masa tindakbalas pada 40, 60 dan 80 (minit); dan nisbah methoxide:minyak sawit iaitu 4:1, 6:1 dan 8:1. Untuk setiap eksperimen yang dilakukan, minyak mentah sawit dirawat dengan magnesium sulfat untuk mengeluarkan lebihan lembapan air. Kemudian, minyak mentah sawit itu dipanaskan pada suhu 50°C and dicampurkan bersama *methoxide* (kalium hidroksida dan metanol) mengikut parameter yang dikaji. Kelajuan pergolakan ditetapkan pada 250 rpm. Selepas proses *transesterification* lengkap, campuran panas itu dibiarkan tidak kurang dari 12 jam di dalam corong pemisah. Dua lapisan terbentuk iaitu lapisan bawah dikenali sebagai gliserin dan lapisan atas sebagai minyak sawit metil ester. Lapisan minyak sawit metil ester akan dicuci menggunakan air paip bersuhu 70 °C selama beberapa kali. Hasil POME iaitu biodiesel akan dipanaskan di dalam ketuhar pada suhu 50 °C untuk mengeluarkan lebihan air. Kadar optima biodiesel daripada penyelidikan ini menghasilkan 88 % dengan keputusan suhu tindakbalas optima adalah 60 °C, masa tindakbalas optima adalah 60 minit dan nisbah *methoxide*:minyak adalah 6:1. Berdasarkan keputusan itu, 500 mL biodiesel telah dihasilkan untuk digunapakai dalam analisis ciri-ciri fizikal biodiesel tersebut. Analisis yang dilakukan ke atas biodiesel ini memperoleh nilai ketumpatan 876.0 kg/m^3, kelikatan kinematik 4.76 mm^2/s, nilai *cetane* 62.8, *flash point* 170 °C , *cloud point* 13 °C dan nilai saponifikasi 206.95 mg/L. Ciri-ciri fizikal biodiesel yang dianalisa ini telah membuktikan bahawa nilai-nilai itu diterima dan masih lagi merangkumi ASTM D6751 dan European Standards.

Kata kunci: Biodiesel, minyak sawit, base catalyzed, transesterification

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LIST OF ABBREVIATIONS

FFB	Fresh Fruit Bunches
POME	Palm Oil Methyl Ester
PO	Palm Oil
CPO	Crude Palm Oil
KOH	Potassium Hydroxide
MetOH	Methoxide
$MgSO_4$	Magnesium Sulphate
PORIM	Palm Oil Research Institute of Malaysia
O&GJ	Oil and Gas Journal
FAME	Fatty Acid Methyl Ester
USDA	U.S. Department of Agricultural
ASTM	American Society of Testing and Materials
SVO	Straight Vegetable Oil
EPAct	Energy Policy Act

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CHAPTER 1

INTRODUCTION

1.0 BACKGROUND OF STUDY

The demand of energy has increased rapidly with growing of world population. The reserves of fossil fuel are being depleted, while the environmental problems caused by their use became serious issue. Thus, the renewable energy has been promptly developed (Manh et al., 2011; S. Mori, 2009; and Werther, 2009). Among the various alternative fuels being developed, the biodiesel has received special attention because it is easy to produce from available and renewable sources (vegetable oils and animal fats), safe to handle and use, eco-friendly, and miscible with petroleum diesel in all proportional for use in existing diesel engines without modification (Tyagi et al., 2010).

Considering the problems faced by agriculture in which the products market ability is limited and much of the land is not utilized as in the case in many countries nowadays, agriculture should be directed to the invention of new alternative products. Biodiesel industry would have a significant beneficial impact on agriculture and rural communities. It would provide an outlet for excess vegetable oil crops and land currently being used to produce surplus crops could be switched to oilseeds to provide additional feed stock for biodiesel (Gerpen et al., 2007).

This research presents the experimental expectation to visually determine the physical properties of biodiesel produced from palm oil. This biodiesel is defined as the alkyl ester of palm oil also known as palm oil diesel.

Palm oil is an extremely versatile commodity which traditionally has been used both as food stuff and as a raw material in non-food items such as cosmetics, soaps, shampoos and washing detergent. Only recently, with rising mineral oil prices and challenges from climate change, there have been calls for palm oil to be used as a renewable energy source. Like any other vegetable oils, palm oil can be used as a fuel in vehicles or for electricity or heat generation (Reinhardt et al., 2007). Due to increasing global needs to reduce dependence on fossil fuel, palm oil biomass offers great potential as a cost-effective feed stock for biodiesel. In this capacity, it is capable of reducing carbon dioxide emission by more than 80%. Therefore, biodiesel is seen as an approach to reduce the impact of the greenhouse effect by 41-57% and as a way diversifying energy supplies to support national energy security plans (Balat & Balat, 2010; Rao et al., 2011).

Biodiesel is produced by the chemical transformation of vegetable oils or animal oils into the corresponding long-chain fatty acid alkyl esters. This transformation is carried out by the transesterification of large, branched triglycerides in oil with a lower alcohol in the presence of an acidic or a basic catalyst (Tyagi et al., 2010). One benefit of this chemical conversion is that these esters have similar properties as the mineral diesel fuel and even better in terms of its *cetane* number (Balat & Balat, 2010; Knothe, 2010). The *cetane* number is related to the time that passes between injection of the fuel into the cylinder and onset of ignition (Predojevic, 2008; Nagi et al., 2008).

Malaysia is the second palm oil producer, therefore Malaysia in the past have focused on palm oil as raw stock used for biodiesel production (Mekhilef et al., 2010) and due to the higher prices of fuel and increasing demand for alternative renewable energy in Western World. In 1983, the Palm Oil Research Institute of Malaysia (PORIM) successfully converted crude palm oil to palm oil methyl ester (POME) through transesterification (Musa, 2010).

1.1 PROBLEM STATEMENT

Depletion of petroleum is an urgent problem need to be solved and it led to much attention on producing biodiesel. Some countries including Malaysia decided to look for bio-based alternative energies which lead to the rising in demand for bio-based feed stocks such as palm oil and rapeseed oil. Therefore, this study is important to check the properties of bio-based fuel to be an alternative for the fossil fuel compared to the standard properties that can be accepted worldwide.

1.2 OBJECTIVES

a) To produce biodiesel from palm oil
b) To analyse the physical properties of biodiesel produced from palm oil (PO) and compare to standard properties.

1.3 SCOPE OF STUDY

The scopes of this study are finding the alternative to fossil fuel from natural resources and the use of vegetable oil which is palm oil for biodiesel production.

1.4 RATIONAL AND SIGNIFICANCE

According to Oil and Gas journal (O&GJ), the estimated worldwide reserves of fuels at the beginning of 2004 were 1.27 trillion barrels of oil and 6,100 trillion cubic feet of natural gas (Briggs and Vasudevan, 2008), which is proven recoverable reserves. At today's consumption level of about 85 million barrels per day of oil and 260 billion cubic feet per day of natural gas, the reserves represent 40 years of oil and 64 years of natural gas. The growing economic risk of relying primarily on fossil fuels with sources, clean and renewable bio fuels has been known as the answer to the issue of diminishing fossil fuels (Nagi et al., 2008).

Nowadays, the world-wide palm oil market is increasing and this is mainly because of the growing production of biodiesel. The rising prices are bad news to biodiesel producers who rely on palm oil for their feed stock, unless the biodiesel producer happens to be the producer of the palm oil itself. This is one of major reasons why investment in palm oil-based biodiesel refineries is being led by palm oil producers. Based on few criteria, palm oil is the most potential vegetable oil which can be used as raw material to manufacture biodiesel. On the other hand, the usage of palm oil consider to be the most wanted palm oil products for its cheap price, consume low energy and readiness for downstream processing (Khalid and Khalid, 2011).

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL

2.1.1 Introduction to Biodiesel

In the last few years, against the background of increasing concerns regarding the energy supply security as well as environmental concern has increased the interest for renewable energy sources (Borges & Diaz, 2012). This have resulted in some countries to look for bio-based alternative energies which lead to the increase in demand for bio-based feed stocks such as palm and rapeseed oil (for biodiesel) and sugar cane and corn (for ethanol). Due to the increased importance of biodiesel in Malaysia and elsewhere, the impact of this new demand has added a new dimension in the fats and oils market particularly palm oil (Applanaidu et al., 2010).

Biodiesel is a clean burning alternative fuel that comes from 100 % renewable resources such as natural vegetable oils and fats. Biodiesel is made through a chemical process which converts oils and fats of natural origin into fatty acid methyl esters (FAME) that can be used in any diesel engine without modifications. Chemically, it is defined as mono alkyl esters of long chain fatty acids derived from renewable lipid sources (Sagiroglu et al., 2011).

As stated by (Yee et al., 2009), biodiesel also known as biofuel which is biodegradable non-toxic, and typically produces about 60 % less net carbon dioxide emissions than petroleum-based diesel, making it relatively safe and easy to process. Many people confident that biodiesel is the fuel of the future, considering it as energy that could be locally-produced, used and controlled. Biodiesel is gradually gaining acceptance in the market as an environmentally friendly fuel and the demand is expected to increase sharply as an alternative renewable energy source in the near future (Mahlia et al., 2010).

In first half of year 2009 alone, Malaysia exports almost 150,000 tonnes of palm oil biodiesel to other countries as shown in Figure 2.1 (Mekhilef et al., 2010).

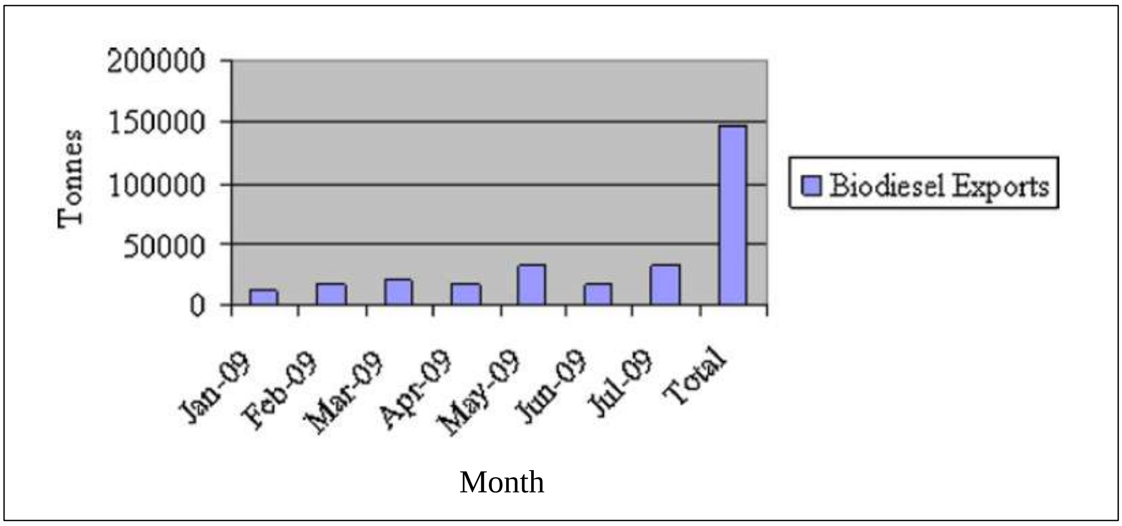

Figure 2.1: Malaysian biodiesel exports (January – July, 2009)

Malaysia exports palm oil biodiesel to several countries like European Union (EU), United States (US), Singapore, Taiwan and other countries as shown in Figure 2.2. European Union has increasing demand for biodiesel; therefore it is important for Malaysia to capture the EU market to become top palm oil biodiesel exporter (Mekhilef et al., 2010).

The development of the oil palm sector in Malaysia is best described as having been most colourful. The growth of the palm oil industry in Malaysia has been phenomenal over the past 30 years. From merely 400 ha planted in 1920, the hectarage increased progressively to 54,000 ha by 1960 (Abdullah et al., 2009). Figure 2.3 shows the cultivated area for oil palm in Malaysia which is divided into three categories of Peninsular Malaysia, Sabah and Sarawak within the next four decades. As noted, the total land fertilized for oil palm plantation shows dramatic rise within these years. In Sabah and Sarawak, the drastic increase in the 1990s can be attributed to the government policy in the intensification of palm oil industries in East Malaysia (Butler, 2005).

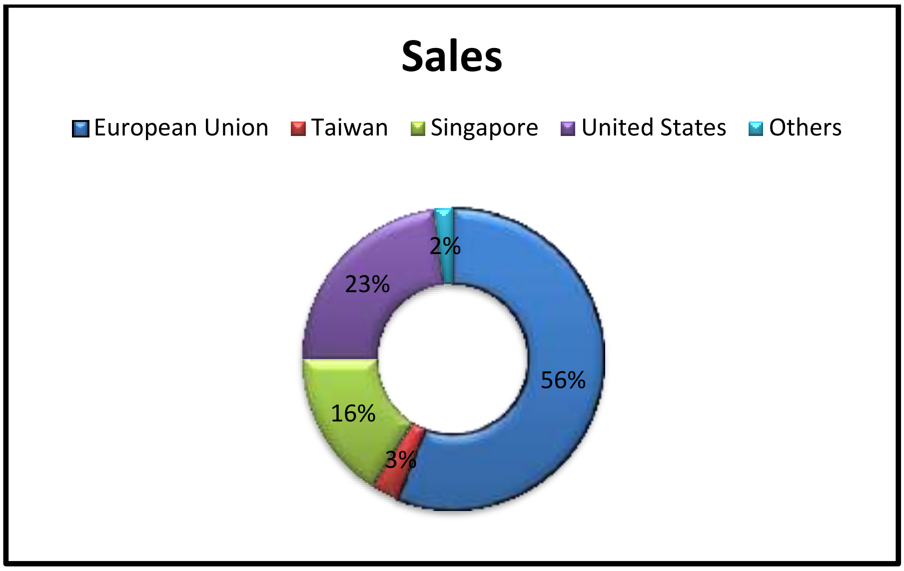

Figure 2.2: Malaysian biodiesel export destinations

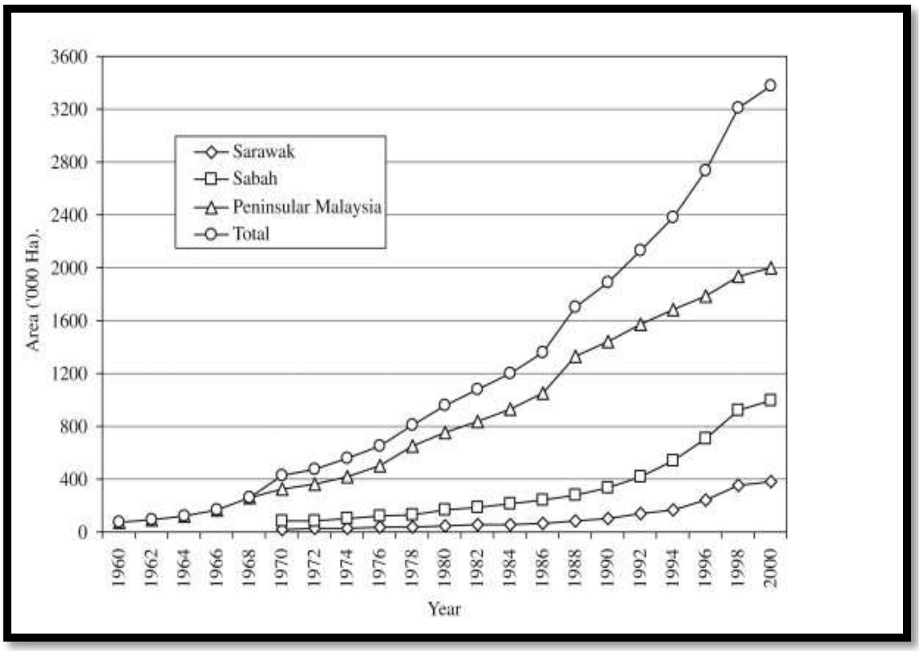

Figure 2.3: Cultivated area for palm oil in Malaysia (1960-2000)

However, Malaysia is currently in danger of being marginalised as our natural competitive advantages diminish. Nations such Indonesia with the resources, capabilities and ambition to grow their domestic palm oil industry are beginning to catch up and threaten our position as a palm oil market leader. From Figure 2.4, it is seen that Indonesia has surpasses Malaysia in production of palm oil and now is the world leader (Butler , 2008).

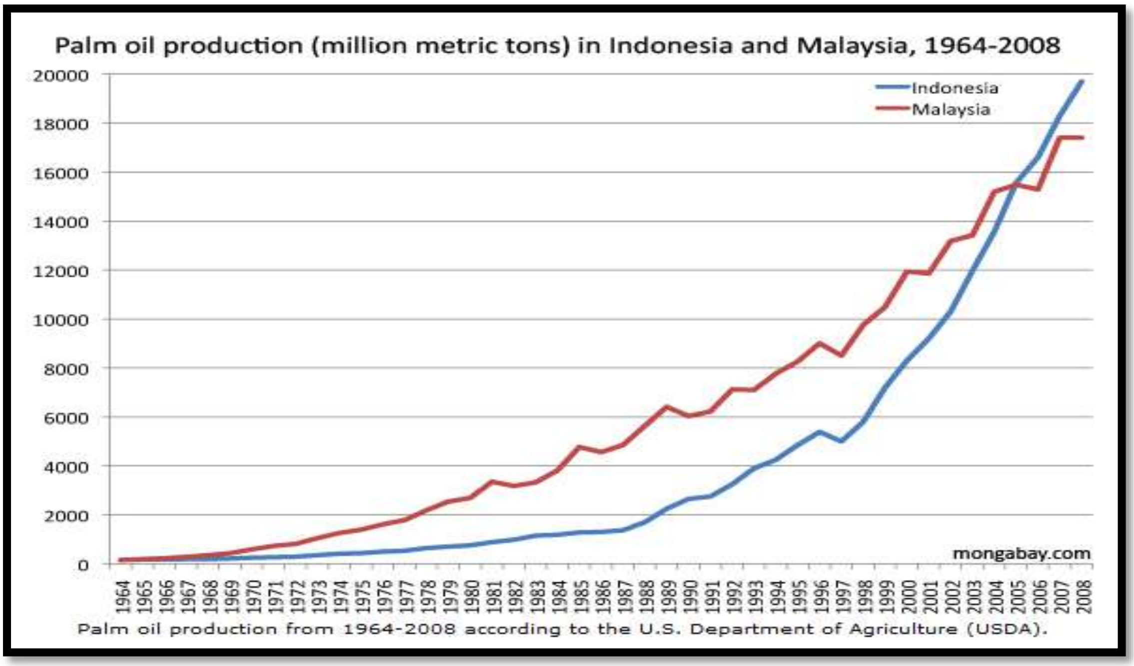

Figure 2.4: Palm oil production from 1964-2008 according to U.S. Department of Agriculture (USDA)

2.1.2 Early History of Biodiesel

The process to produce fuel from fats is not a new process. The history started in the 1880s, when Rudolph Diesel designed a single 10 feet iron cylinder with a flywheel at its base in Augsburg, Germany on August 10, 1893. Later, he designed the compression engine for the World Exhibition in Paris, France. Diesel demonstrated his engine using a common substance, peanut oil. He believed that this form of fuel can be one of the sources needed (Sharma & Singh, 2008). During that era, steam engines were run by coal and processed oils. However, Diesel intended to show that there was a far better method than using biomass fuel. Away in 1912, Diesel has long predicted that the use of vegetable oils for engine fuels would one day become as important as petroleum and the coal-tar products of the present time (Lin et al., 2011).

There were few individuals in the engine industry believed on Diesel's prediction. Henry Ford had created a factory producing mass bio fuels, he believed that this power was perfect in every way and wanted to create all of his automobiles that accepted this fuel. However, in the 1920s, diesel engine manufacturers decided to modify their engines using lower viscosity fossil fuel known as petro diesel.

2.1.3 Biodiesel as an Alternative Source for Fossil Fuel

The term "biodiesel" has its specific and technical definition approved by the American Society of Testing and Materials (ASTM). According to its general definition stated that, "Biodiesel is a domestic, renewable fuel for diesel engines derived from natural oils like soybean oil, and meet the specifications of ASTM D 6751" (Balat and Balat, 2010). Biodiesel can be used in any concentration with petroleum-based diesel fuel in any types of diesel engine. Biodiesel is not the same thing as raw vegetable oil, also known as Straight Vegetable Oil (SVO). To produce biodiesel, vegetable oils or animal fats with short chain primary alcohols such as methanol or ethanol are used as feed stock. It is produced by a chemical process called transesterification by removing glycerine from the oil. Triglycerides in oils or fats can have chemical reaction with the alcohols under suitable conditions (Permsuwan et al., 2011).

Based on its technical definition, biodiesel is defined as the mono-alkyl ester of natural fatty acids produced via transesterification of fats and oils. It is made mainly from renewable biological resources (vegetable or animal fats and oils) and is therefore an ecologically friendly alternative to petroleum-based diesel. Biodiesel fuel is adapted to the diesel engine and may be used in standard diesel engines (Blagoev et al., 2008). In this process, biodiesel is called methyl ester if the alcohol used is methanol and called as ethyl ester if ethanol is used. Usually, methanol is preferable because it is much cheaper than ethanol (Knother, 2010). Meanwhile commonly used catalysts are potassium hydroxide (KOH) or sodium hydroxide (NaOH).

Like petroleum diesel, biodiesel operates in compression-ignition engines. Biodiesel is most often blended with petroleum diesel in ratios of 2% (B2), 5% (B5), and 20% (B20) or as pure biodiesel (B100) (Briggs & Vasudevan, 2008). This blending process of biodiesel and petroleum diesel gives more benefits because it runs in any conventional, unmodified diesel engines. (Gerpen, V.J et al., 2007) reported that B2 is of interest because of its lubricity benefits. Meanwhile, B20 qualifies for fleet compliance under the Energy Policy Act (EPAct) of 1992 helps reduce engine emissions in addition to improved fuel lubricity. B100 provides provides complete replacement of petroleum diesel if the biodiesel could be supplied in sufficient amounts with an affordable cost.

Biodiesel operated on diesel engines produce lower emissions of carbon monoxide, unburned hydrocarbons, and particulate matter and air toxics than operated on petroleum-based diesel fuel. Table 2.1 gives a comparison of palm biodiesel and petroleum diesel based on their characteristics.

Table 2.1: Physical-chemical properties of palm biodiesel and petroleum diesel (Nagi et al., 2008)

Characteristics	**Palm biodiesel (palm methyl ester)**	**Petroleum diesel**
Type of source	Renewable	Fossil
Calorific value (MJ/kg)	41.3	46.8
Gross heat of combustion (KJ/kg)	40.135	45.8
Cetane level	65	53
Flash point (°C)	174.0	98.0
Pour point (°C)	16.0	15.0
Cloud point (°C)	16.0	18.0
Density at 40°C (kg/L)	0.855	0.823
Viscosity at 40°C (cST)	4.5	4.0
Sulphur content (wt. %)	0.04	0.10
Carbon residue (wt. %)	0.02	0.14

2.2 PRODUCTION OF BIODIESEL FROM CRUDE PALM OIL

2.2.1 Raw Stock for Biodiesel

According to (Singh & Singh, 2009), there are several sources which are used as feed stock for biodiesel production such as: soybean, sunflower, palm, canola, cotton seed, Jathropa, rapeseed and soybean oil. However, compared with other vegetable oil, palm oil has far better advantage and potential as feed stock for biodiesel production. Palm oil is a perennial crop, unlike soybean and rapeseed. Perennial crop means the production of oil is continuous and uninterrupted, though annual production has its seasonal peak and down cycle. Palm plantation has the highest oil yield in terms of oil production per hectare of plantation. Palm oil yield from palm plantation is a factor of ten times higher than oil yield from soybean, sunflower or rapeseeds. According to Figure 2.5 below, palm oil has more yield per hectare than any other crops, which makes it the best source to produce biodiesel (Mahlia et al., 2010).

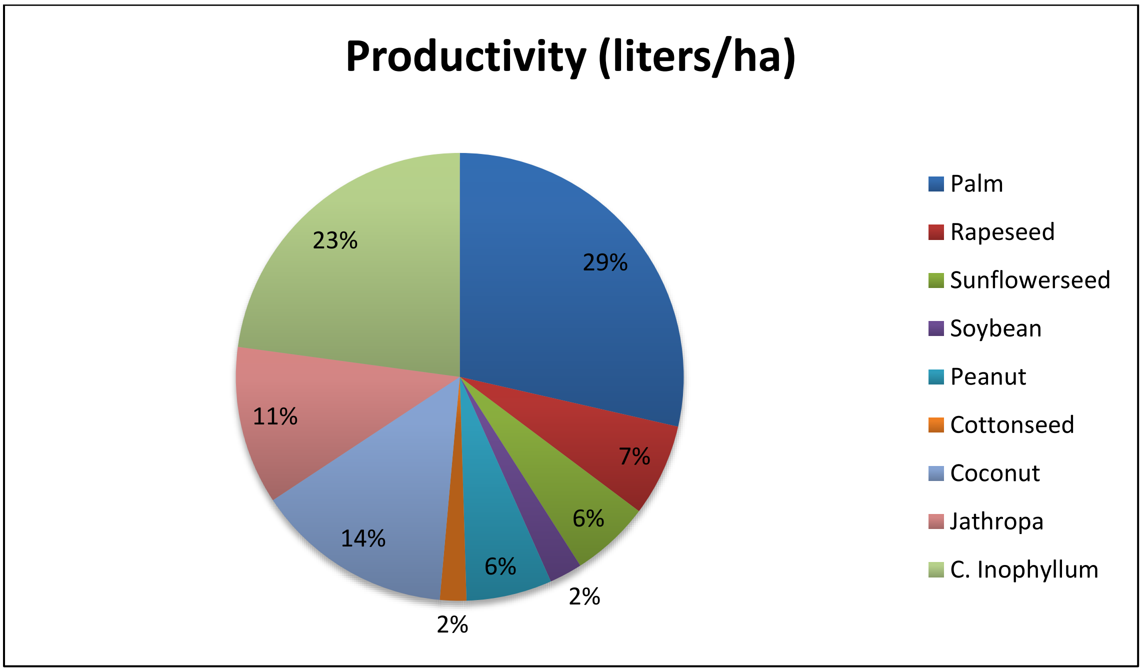

Figure 2.5: Production oil yield for various source biodiesel feed stocks

2.2.2 Palm Oil Processing

Carlsson (2009) reported that palm oil promises the most potential biodiesel feed stock compared to other oil seeds. Palm oil gives higher production yield, low fertilizer, water and pesticides for the plantation. Also, it takes less sunlight in terms of energy balance to produce a unit of oil as it produces more oil per hectare. Palm oil is known for its nutrient fact that makes it suitable as vegetable oil used for daily cooking.

In the process, the Fresh Fruit Bunches (FFB) will undergo some processes in order to separate the palm kernels and palm oil. FFB will be graded according to its ripeness (Mohd et al., 2011). Then, FFB will be transported by cages into the sterilizer to be exposed to steam. The main objective of the sterilisation is to inactive the oil splitting enzyme and to loosen the fruits in the bunch which will make it easier to be removed by shaking or tumbling in the threshing machine (Khalid & Sukaribin, 2009). Later, the fruitlets will be transferred into the digester by using conveyer. Empty fruit bunches will be transported to the empty bunch hopper and used as fertilisers.

In the digester, the palm oil will be released from the fruit by pounding at high temperature which helps to reduce the viscosity of the oil, destroy the *exocarp* and completes the disruption of the oil cells (Amelia et al., 2008). Thus, some palm oil is released and collected in the crude oil tank together with the pressed oil. Also, there is a pressing station to squeeze out the oil from the fibre and remove the nuts.

Nuts will undergo a nut polishing drum and a ripple mill to remove the shells from the kernels (Jekayinfa & Bamgboye, 2006). Kernels will be processed to palm kernel oil, meanwhile the crude palm oil is pumped to a vertical clarification tank for oil separation.

Figure 2.6 shows the simplified step by step process of palm oil transformed into crude palm oil which is then processed into other products including biodiesel (Mekhilef et al., 2010).

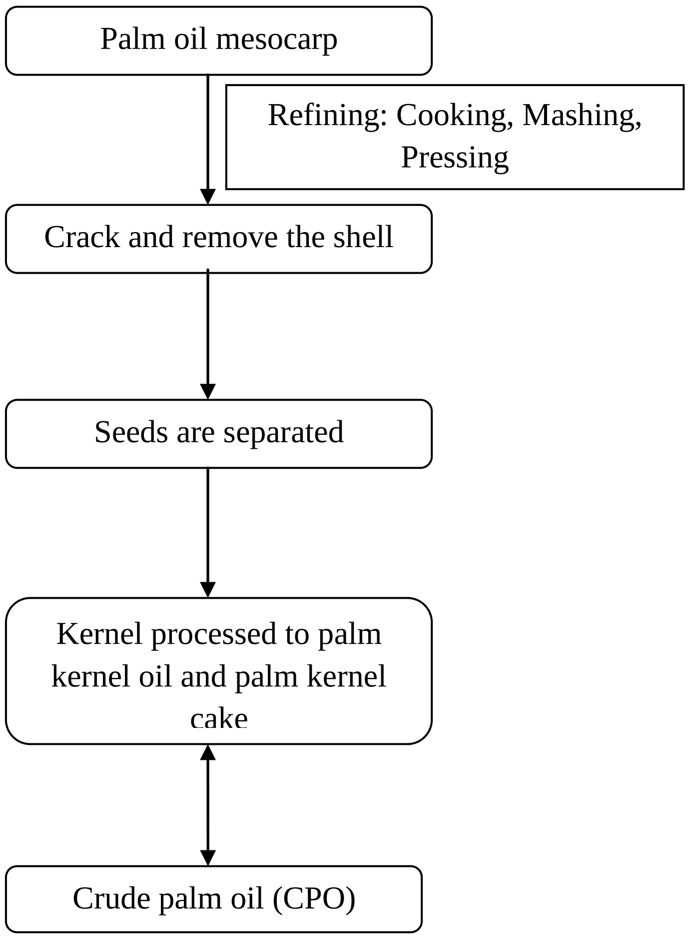

Figure 2.6: Palm plant (crude palm oil process)

The PO is being harvested from palm trees and transported to palm oil refinery to be refined, the palm oil is produced and this output can be converted into methyl ester and directly used as biodiesel. Another method is to blend the refined oil with petroleum diesel to make diesel fuel which is shown in Figure 2.7, this blending process is called Envo Diesel.

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